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Article

Quantifying Uncertainties in Sequential Chemical Extraction of Soil Phosphorus Using XANES Spectroscopy

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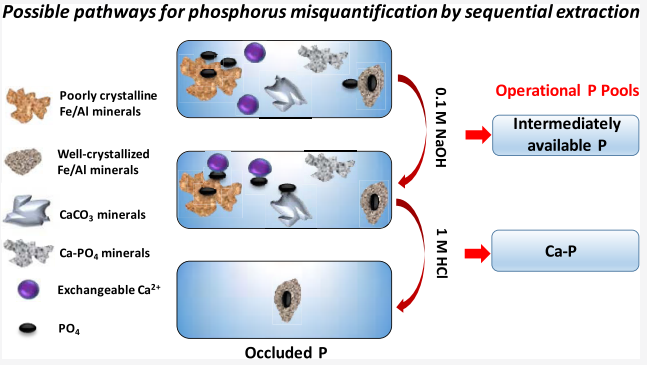
ABSTRACT: Sequential chemical extraction has been widely used to study soil phosphorus (P) dynamics and inform nutrient management, but its efficacy for assigning P into biologically meaningful pools remains unknown. Here, we evaluated the accuracy of the modified Hedley extraction scheme using P K-edge X-ray absorption near-edge structure (XANES) spectroscopy for nine carbonate-free soil samples with diverse chemical and mineralogical properties resulting from different degrees of soil development. For most samples, the extraction markedly overestimated the pool size of calcium-bound P (Ca-P, extracted by 1 M HCl) due to (1) P redistribution during the alkaline extractions (0.5 M $NaHCO_3$ and then 0.1 M NaOH), creating new Ca-P via formation of Ca phosphates between NaOH-desorbed phosphate and exchangeable Ca^{2+} and/or (2) dissolution of poorly crystalline Fe and Al oxides by 1 M HCl, releasing P occluded by these oxides into solution. The first mechanism may occur in soils rich in well-crystallized minerals and exchangeable Ca^{2+} regardless of the presence or absence of $CaCO_3$, whereas the second mechanism likely operates in soils rich in poorly crystalline Fe and Al minerals. The overestimation of Ca-P simultaneously caused underestimation of the pools extracted by the alkaline solutions. Our findings identify key edaphic parameters that remarkably influenced the extractions, which will strengthen our understanding of soil P dynamics using this widely accepted procedure.



INTRODUCTION

Phosphorus (P) is a critical nutrient element in soils, and its availability affects terrestrial ecosystem properties, agricultural productivity, and water quality.[1,2] The speciation of soil P is commonly assessed by sequential chemical extraction (SCE), which provides fundamental data for understanding P dynamics and risk of P loss.[3−8] Sequential chemical extraction operationally defines P pools of different chemical stability to infer P bioavailability by using chemical reagents of increasing strength to sequentially extract P from solid samples, such as soils, sediments, and aeolian dust.[6,9−11] Many SCE schemes have been developed,[12−16] typically using acidic and alkaline extractants to separate iron and aluminum-bound P (Fe/Al-P) and calcium-bound P (Ca-P).[17−20] In particular, the modified Hedley fractionation scheme is among the most widely used for soils (Figure 1),[3,4,6,15,21] with sufficient information available to allow the creation of global maps of soil P fractions.[5]

Despite their widespread use, SCE schemes suffer from a number of uncertainties that can limit the insight obtained from these procedures. The P fractionation derived from the modified Hedley extraction scheme may be uncertain because the chemical identity of each P pool remains ambiguous and because P can redistribute among different solid phases during extractions.[22] For example, during the 0.1 M NaOH extraction of $CaCO_3$-bearing soils, P desorbed from mineral surfaces, particularly Fe and Al oxide surfaces, can readsorb on $CaCO_3$ surfaces, forming new Ca-P that is subsequently removed as Ca-P by the following 1 M HCl extraction.[23] Such redistribution of P species leads to overestimation of Ca-P and underestimation of NaOH-extractable Fe/Al-P.[23] In addition, Hedley et al. speculated that 1 M HCl can extract some Fe/Al-P, causing overestimation of Ca-P as well.[13] However, most subsequent studies have assumed that Fe/Al-P was insoluble in 1 M HCl and thus define 1 M HCl extractable P exclusively as Ca-P.[15,19,24,25]

Phosphorus K-edge X-ray absorption near-edge structure (XANES) spectroscopy has been increasingly used to determine soil P speciation.[11,26−29] A few studies have compared XANES spectroscopy to the modified Hedley SCE

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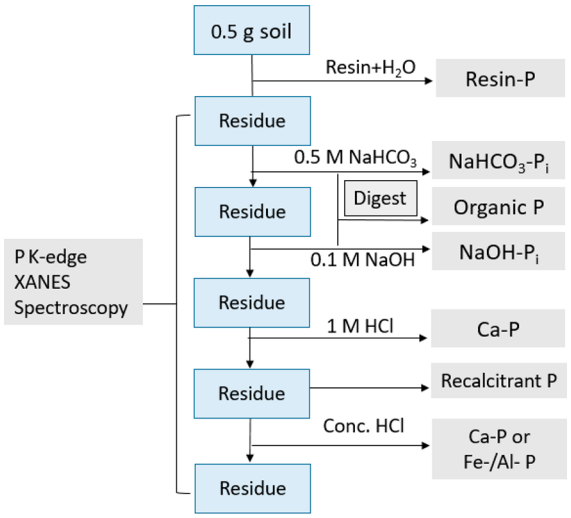

Figure 1. Flow chart for modified Hedley fractionations combined with phosphorus K-edge X-ray absorption near-edge structure (XANES) spectroscopic analysis.

in characterizing soil P composition.[26,28,30−32] Some XANES studies found that for organic amendments, biosolid-amended calcareous soils and peat soils, the Ca-P and organic P fractions derived from the two methods were comparable and that the identities of the P removed by 0.1 M NaOH and 1 M HCl were consistent with the assignments of Hedley and its modified protocol.[30−32] However, others showed that the modified Hedley extraction scheme significantly overestimated Ca-P in volcanic soils in Arizona (61−65% by SCE versus 16−37% by XANES spectroscopy) and Hawaii (11−28% by SCE versus 0% by XANES spectroscopy).[26,28] The different conclusions of those previous studies may be caused by different soil properties, although the specific soil properties remain unknown.

The objectives of the present study were to identify the mechanisms underlying potential misquantification associated with the modified Hedley extractions and assess whether these mechanisms depend on soil properties. We used P K-edge XANES spectroscopy to characterize the speciation of P in the extraction residues for soils from two 3 million year old semiarid soil chronosequences. This analysis is meant to determine whether P redistribution occurs during the $NaHCO_3$ and NaOH extractions. It also provides an understanding of the speciation of P extracted by the major extraction steps, such as dilute and concentrated HCl extractions. Due to different developmental stages and aeolian dust inputs,[28] these soils varied widely in physiochemical and mineralogical properties, providing an excellent study system for evaluating how soil properties influence the accuracy of SCE.

MATERIALS AND METHODS

Study Sites, Soil Sampling, Pretreatments, and Properties. Two 3 million year old soil chronosequences, the substrate age gradient of Arizona (SAGA) and the Merced chronosequence, were located in the San Francisco volcanic field in northern Arizona and Central Valley in California, respectively. The substrate age ranged from 1000 years (1 ky) to 3000 ky for SAGA and 0.1−3000 ky for Merced, while the other four soil formation factors were similar within each chronosequence.[1,33] Both chronosequences were located in a semiarid environment.[1,33] The parent material at the Merced sites was dioritic to granitic sand deposits from glacial outwash[34,35] and was microporphyritic basalt at the SAGA sites.[1] Surface soils (0−15 cm) were collected, air-dried, homogenized, ground, and passed through 100 mesh and preserved under dark and dry conditions. The same soil samples were used in previous studies,[28,32,34] and more detailed information about the study sites, soil sampling, and pretreatments can be found in previous publications.[28,32,34]

Some soil chemical properties are listed in the Supporting Information (Table S1) to assist in data interpretation of the present study, including exchangeable Ca^{2+} concentrations, pH, bulk densities, and contents of poorly crystalline (Fe_{ox} and Al_{ox}) and well-crystallized (Al_{di} and Fe_{di}) Fe/Al oxides. All of these values were reported previously[1,28,33] except for pedogenic Fe/Al fractions of Merced chronosequence and exchangeable Ca^{2+} of both chronosequences, which were measured in the present study (Text S1). Carbonates were absent in the surface soils of both chronosequences.[1,33]

Modified Hedley Sequential Chemical Extraction. Soil P pools were quantified using the modified Hedley SCE (Figure 1).[15] Selmants and Hart[1] previously conducted the extractions on the same but field moist SAGA soil samples (<2 mm, unground). To be consistent with P K-edge XANES analyses in the present study, we re-did the extractions with the air-dried and ground soils.[36]

Each pretreated soil sample (~0.5 g) was sequentially extracted in triplicate with one anion exchange membrane strip in deionized (DI) water, 0.5 M $NaHCO_3$, 0.1 M NaOH, 1 M HCl (D-HCl), and concentrated HCl (C-HCl). The detailed procedures are provided in Text S2. In addition, the Fe, Al, and Ca concentrations in the HCl extract were also measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES) to explore the correlations between P and these major cations in the extract. The intermediately available inorganic P (P_{int}), organic P (P_o), Ca-P, and occluded P (P_{occ}) pools were defined as the sum of $NaHCO_3-P_i$ and $NaOH-P_i$, the sum of $NaHCO_3$-P_o and NaOH-P_o, D-HCl-P, and P in the D-HCl extraction residue, respectively.[1,37−39] The P_i removed by $NaHCO_3$ and NaOH was of essentially similar chemical nature and may be regarded as extractable Fe/Al−P.[19] These assignments, however, are rather arbitrary. For example, C-HCl-P was also included as a part of Ca-P previously.[1]

Phosphorus K-Edge XANES Spectroscopy. The XANES spectra of all extraction residues, which were prepared in additional sequential extraction experiments, as well as of the raw Merced soils, were collected in fluorescence mode at the soft X-ray micro characterization beamline (SXRMB) at the Canadian Light Source, Saskatoon, Canada. The NaOH and HCl extraction residues were washed with DI water three times and freeze-dried before the analysis. The results of P K-edge XANES analysis of the raw SAGA soils were reported in our previous study.[28] Detailed information about data collection is provided in Text S3.

The spectra of the extraction residues were processed in two ways, depending on whether P redistribution occurred during the extractions. In the first approach, the XANES spectra of the residues were subject to the linear combination fitting (LCF) analysis with a pool of P reference XANES spectra to determine the P speciation. The difference in P speciation in the residue soils before and after the extraction provided information regarding whether and how the extraction altered the P speciation of the residue soils (i.e., P redistribution). Any

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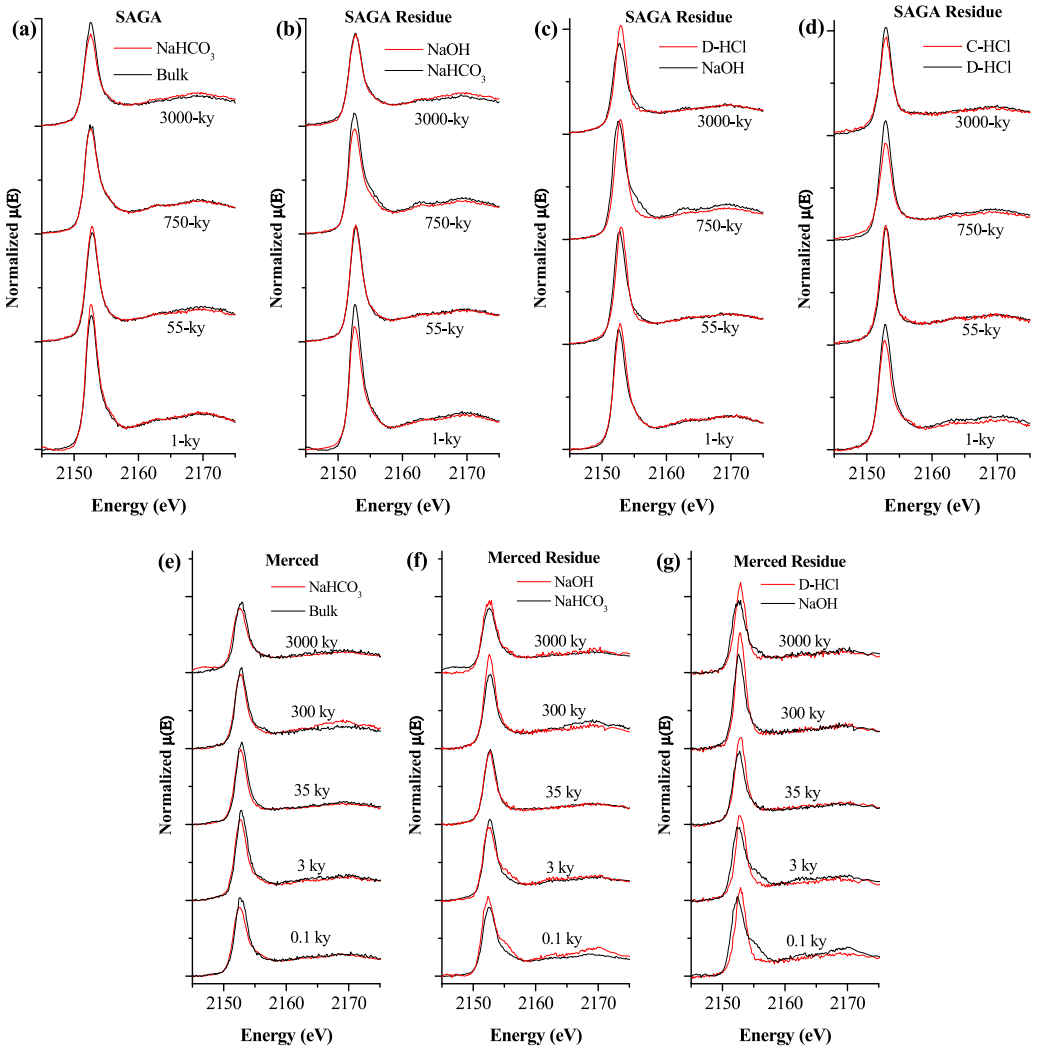

Figure 2. Comparisons between P K-edge XANES spectra of the residues before and after each major extraction step for SAGA (a-d) and Merced (e-g) chronosequences. The spectra of hot concentrated HCl (C-HCl) residues for the Merced soils were not presented here due to their poor spectral quality. D-HCl: 1 M HCl.

redistribution could impact the P removed in the subsequent step.

In a second approach, the difference spectra between the spectra of a soil residue before and after the extraction were obtained and then linear combination fitted to get the speciation of the P removed by the extraction from the soil.[30] To obtain the difference spectra, the bulk spectra of the residues were pre-edge background-removed without post-edge normalization. Then, the whiteline peak height of each residue spectrum was normalized based on the proportion of the total residual P over the total P concentration of the raw soil. The difference spectra were obtained by subtracting the concentration-normalized spectra of two successive extraction steps from each other. The obtained difference spectra were further subject to background removal, post-edge normalization, and the LCF analysis for P speciation characterization. The adoption of difference spectra between two successive residue spectra can directly show the speciation of P removed by a given extraction. By doing this, we assumed that the extraction only removed certain P species but did not change the P species remaining in the solid. Thus, this approach did not work for samples that had P redistribution during the extractions, which would distort the difference spectra.

Five reference spectra were used in the LCF analysis, including phytate, hydroxyapatite, calcium dihydrogen phosphate monohydrate [$Ca(H_2PO_4)_2{\cdot}H_2O$], and phosphate adsorbed on amorphous Al hydroxides and ferrihydrite (Figure S1).[28] Hydroxyapatite and $Ca(H_2PO_4)_2{\cdot}H_2O$ were combined to approximately represent the entire Ca-P pool without further distinguishing them in the results to avoid potential overinterpretation. These P references can well represent the major P species in the residues and the P removed by the extractants. The goodness of LCF was indicated from the *R*-factor that was reported along with the results. *R*-factors were smaller than 0.01 for most of the samples, indicating good fits. However, due to the low total P concentrations and the increased quartz contents of C-HCl extraction residues for some soils, their XANES spectra were too noisy to be fitted reliably.

Phosphorus K-edge XANES analyses are subject to multiple uncertainties caused by sample preparation and data analyses. For example, the uncertainty of LCF-derived percentages was about 10%,[40] thus P species representing less than 10% is doubtful.[28] It might also be challenging to differentiate adsorbed P_o and P_i species due to their sometimes similar spectra, and SCE could be more accurate than XANES

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Table 1. XANES-Derived Changes in Ca-P Concentrations before and after the $NaHCO_3$ and NaOH Extractions for SAGA and Merced Soils[a]

	total Ca−P (mg/kg)					
site (ky)	raw soil (A)	$NaHCO_3$ residue (B)	NaOH residue (C)	B/A	C/B	C/A
			SAGA			
1	637 (72)	673 (13)	689 (24)	1.1 (0.1)	1.0 (0.02)	1.1 (0.1)
55	251 (62)	219 (4)	287 (6)	0.9 (0.2)	1.3 (0.05)	1.1 (0.2)
750	400 (34)	368 (20)	366 (8)	0.9 (0.0)	1.0 (0.03)	0.9 (0.1)
3000	78 (16)	144 (8)	110 (3)	1.9 (0.2)	0.80 (0.02)	1.4 (0.2)
			Merced			
0.1	209 (40)	463 (28)	517 (27)	2.2 (0.1)	1.1 (0.0)	2.5 (0.1)
3	133 (42)	378 (30)	432 (28)	2.9 (0.2)	1.1 (0.0)	3.3 (0.3)
35	76 (24)	189 (12)	180 (9)	2.5 (0.3)	0.95 (0.0)	2.4 (0.3)
300	114 (14)	null	141 (9)	−	−	1.2 (0.6)
3000	141 (25)	202 (6)	226 (11)	1.4 (0.2)	1.1 (0.0)	1.6 (0.1)

[a]The values in the parentheses were standard errors. "−" means that the LCF analysis was not conducted on these samples due to their poor spectra. A, B, and C represent the Ca-P concentrations in the raw soils and the residues after $NaHCO_3$ and NaOH extractions, respectively. The Ca-P concentrations in the bulk soils and extraction residues were calculated by multiplying the total P concentration with the XANES-derived Ca-P proportion in each sample (Table S4).

spectroscopy for determining P_o concentrations.[41] Moreover, the particle size (<0.15 mm) of 100-mesh ground soils was larger than the X-ray penetration depth and thus XANES spectra might not be able to reflect the speciation of the entire P pool,[42] while other studies used similar or even bigger particles sizes of soils.[31,43] However, P K-edge XANES spectroscopy, used with cautiousness, is the most powerful approach for soil P speciation analysis.

RESULTS

Soil Chemical Properties. These soils differed markedly in chemistry and mineralogy, due principally to different parent materials and degrees of chemical weathering. All soils were weakly acidic (4.7−6.8), consistent with the absence of carbonates (Table S1).[1,33] SAGA soils contained relatively high Fe_{ox} (1.61−17.25 g/kg) and Al_{ox} (3.39−8.10 g/kg),[28] particularly in the two younger soils, compared to Merced soils (Fe_{ox}: 1.25−3.74 g/kg; Al_{ox}: 0.54−1.04 g/kg). The concentration of exchangeable Ca^{2+} differed up to 13-fold in SAGA (0.38−5.02 g/kg) and Merced (1.17−4.04 g/kg) soils (Table S1). Based on X-ray fluorescence (XRF) measurements, the total P concentrations in the bulk soils were 502−1755 mg/kg for SAGA and 513−1420 mg/kg for Merced (Table S2).

Hedley Fractionation. The concentration of P removed by each extraction step is given in Table S2. The derived P_{int}, Ca−P, P_{occ}, and P_o pools contributed 3.7−14, 24.6−56.1, 0.7−7.6, and 36.4−54.6%, respectively, to total P for SAGA soils and 8.3−34.7, 25.7−62.1, 14.9−47.9, and 2.5−19.1%, respectively, for Merced soils (Figure S2). The SCE recovered 87−112% of total soil P (Table S2). Our SCE results were consistent with those in Selmants and Hart,[1] which used the same but field moist and unground soils.

Phosphorus Speciation by XANES Spectroscopy in Raw Soils. The soil P speciation varied markedly for both chronosequences. The XANES LCF analysis showed that Ca-P, (Fe + Al)-P, and P_o contributed 16−39, 48−82, and 1−23%, respectively, to soil total P of SAGA and 66−85, 12−25, and 2−18%, respectively, to soil total P for Merced soils (Figure S2). The relative proportions of Ca-P between samples were consistent with the spectral features of Ca-P, in which higher Ca-P corresponded to a lower energy position of the whiteline peak, a stronger shoulder on the right side of the whiteline and stronger splitting of the post-edge peak (Figure 2). The proportions of P_o from SCE were lower than (for SAGA) or comparable to (for Merced) the XANES results. The lower P_o proportions were probably caused by the incomplete extraction as indicated by the presence of P_o in the P_{occ} pool (Table S2). The uncertainties associated with the LCF analysis may also have contributed to the lower values. In contrast, remarkable differences in Ca−P proportions between SCE and XANES were observed for SAGA and Merced soils, e.g., in the SAGA soils, 25.7−62.1% from SCE versus 66−85% from XANES spectroscopy. The LCF analysis on the D-HCl difference spectra and the residue spectra below provided the mechanisms for the discrepancies.

Phosphorus Speciation in Extraction Residues. A comparison of P K-edge XANES spectra of the extraction residues before and after each extraction step provided insights into how the extraction might have changed the P speciation in the residues. Due to the fact that a small portion of the total P was removed by resin + DI water, the spectra of the residues after the extraction were almost the same as those of the raw soils (data not shown). Considering the uncertainty (~10%) of the XANES LCF analysis, the analysis was not conducted on the spectra of the resin-extraction residues. All XANES spectra of the residues after $NaHCO_3$, NaOH, or HCl extractions were linear combination fitted for most of SAGA and Merced soils (Figures S3 and S4), except for those of low spectral quality (Figure S5).

Phosphorus Speciation in $NaHCO_3$ and NaOH Extraction Residues. The concentration of Ca-P in each residue was obtained by multiplying the P proportion by total P concentration in the residue so that one can compare the Ca-P concentration before and after each extraction. The comparison provides information on whether the extraction caused P redistribution, such as redistribution from the Al/Fe-P pool to the Ca-P pool.

For each SAGA soil, the spectra of the $NaHCO_3$ residue and raw soils differ significantly only for 3000-ky soil (Figure 2). After the $NaHCO_3$ extraction, the XANES whiteline position shifted toward lower energy, indicating increased Ca-P proportion.[28] Consistently, the LCF analysis showed that the Ca-P proportion increased from 16% in the raw soil to 36% in the extraction residue (Table S3), with corresponding changes

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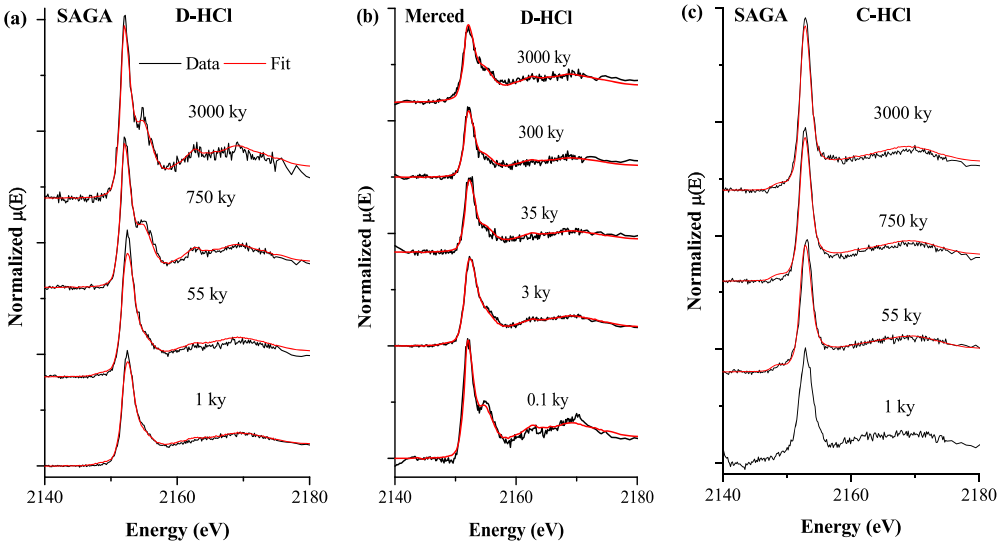

Figure 3. Phosphorus D-HCl difference XANES spectra, C-HCl difference spectra, and their linear combination fits for SAGA and Merced soils. The spectra reflect the speciation of P removed by 1 M HCl (a, b) and hot concentrated HCl (c), respectively. The C-HCl difference spectrum of the 1-ky SAGA site was not normalized and fitted due to the low spectral quality (c). The C-HCl difference spectra for the Merced sites were not shown here due to their poor spectral quality. D-HCl: 1 M HCl; C-HCl: hot concentrated HCl.

Table 2. Speciation of the P Removed by Diluted HCl (D-HCl) and Hot Concentrated HCl (C-HCl) As Quantified by Linear Combination Fitting of the Difference XANES Spectra of the SAGA and Merced Soils[a]

difference spectra	site age (ky)	Ca-P (%)	Fe-P (%)	AlP (%)	P_o (%)	*R*-factor
			SAGA			
NaOH − D-HCl	1	30 (1)	70 (4)	0 (0)	0 (0)	0.009
	55	45 (3)	55 (9)	0 (0)	0 (0)	0.025
	750	97 (0)	0 (0)	3 (0)	0 (0)	0.009
	3000	100 (0)	0 (0)	0 (0)	0 (0)	0.018
D-HCl − C-HCl	1					
	55	0 (0)	100 (0)	0 (0)	0 (0)	0.018
	750	9 (0)	91 (0)	0 (0)	0 (0)	0.016
	3000	6 (0)	94 (0)	0 (0)	0 (0)	0.014
			Merced			
NaOH − D-HCl	0.1	92 (0)	0 (0)	0 (0)	9 (0)	0.034
	3	43 (1)	28 (2)	17 (1)	12 (0)	0.006
	35	87 (7)	13 (2)	0 (0)	0 (0)	0.038
	300	89 (6)	11 (1)	0 (0)	0 (0)	0.040
	3000	84 (1)	16 (0)	0 (0)	0 (0)	0.027

[a]The standard errors of the linear combination fitting (LCF) analysis were included in the parentheses. *R*-factor is an indicator of the goodness for the LCF analysis on the XANES spectra. P_o: organic P.

of the Ca-P concentration from 78 to 144 mg/kg. Apparently, the $NaHCO_3$ extraction created an additional 90% Ca-P than that of raw soils at the 3000-ky SAGA site (Table 1). Both XANES whiteline peak position and LCF analyses showed that NaOH extraction did not alter Ca-P for SAGA soils except the 3000 ky soil, for which Ca-P was increased by 40% relative to that in the raw soil (Table 1).

The changes of the spectra after the $NaHCO_3$ extraction for Merced soils were more remarkable than for SAGA soils. The whiteline peak of the $NaHCO_3$ residues shifted to lower energy for all Merced soils (Figure 2), indicating significant increases in Ca-P proportion after the extraction. Consistently, the LCF analysis showed that the $NaHCO_3$ extraction created 50−190% additional Ca-P in the residues relative to the raw soils (Table 1).

The NaOH extraction further changed P speciation for 0.1-, 3-, and 3000-ky Merced soils. Compared to the spectra of the $NaHCO_3$-residues, the whiteline peak of the NaOH residues shifted to lower energy and the typical shoulder peak of Ca-P at 2155.5 eV became more pronounced (Figure 2). However, the NaOH extraction only slightly increased Ca-P concentration in the NaOH residues compared to $NaHCO_3$ residues for all Merced soils, although it created additional 60−230% more Ca-P relative to the raw soils (Table 1).

Phosphorus Speciation of 1 M HCl Extraction Residues. Remarkable changes in the XANES spectra of the extraction residues occurred after D-HCl extraction. The whiteline peak of the D-HCl residues shifted markedly to higher energy relative to those of the NaOH residue (Figure 2c,g), and the spectra became similar to those of Fe- and Al-P. The P_{occ} for both SAGA and Merced soils was consistently dominated by (Fe + Al)-P (66−95 and 68−90%, respectively; Table S3). Ca-P was detected only for the 1-ky SAGA (14%) and 3000-ky Merced (17%) soils. Considerable proportions of P_o were

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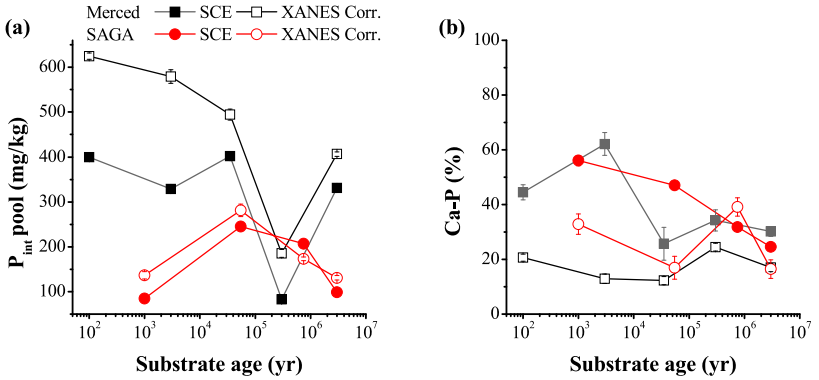

Figure 4. Comparisons between the modified Hedley sequential chemical extraction (SCE) and the P K-edge XANES spectroscopic results for the intermediately available P (P_{int}, $NaHCO_3$−P_i + NaOH−P_i) pool (a) and the Ca-P pool (b) for both SAGA and Merced chronosequence. The corrected intermediately available P pool sizes (XANES Corr.) were also provided, which was obtained by adding the newly created Ca-P by NaOH extraction derived from XANES spectroscopy (Table 2).

Possible chemical reactions involved in the modified Hedley sequential extraction

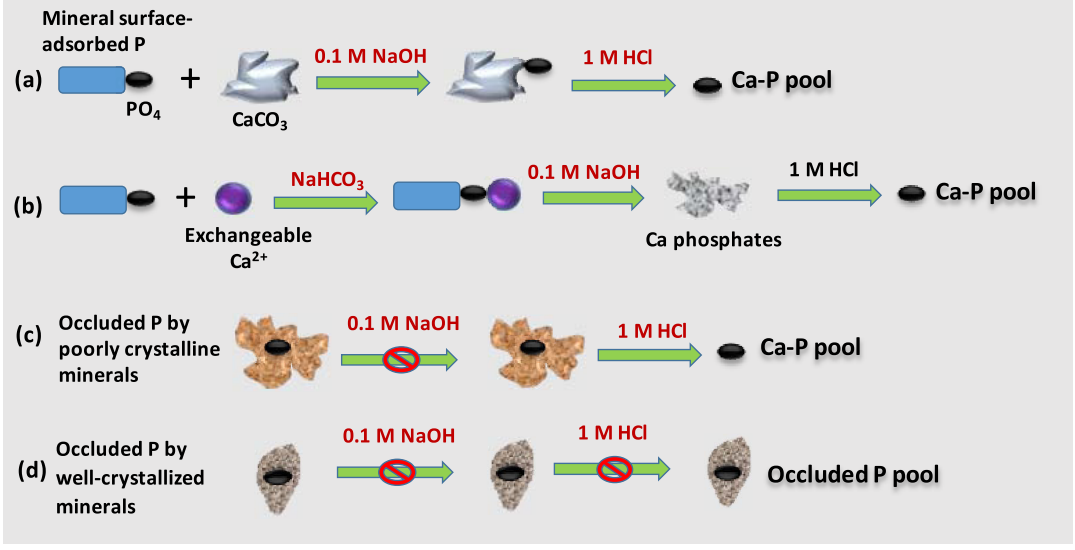

Figure 5. Possible processes (a−c) that can lead to overestimation of Ca-P by modified Hedley sequential fractionations. The forms of Fe- and Al-P, i.e., adsorbed or occluded, by poorly crystalline or well-crystallized minerals, together with the presence of $CaCO_3$ and exchangeable Ca^{2+} in soils, likely determine the misquantification of P fractionated by the modified Hedley protocol. In (a), the overestimation of Ca-P is caused by redistribution of mineral surface-adsorbed P (by either poorly crystalline or well-crystallized Fe/Al-bearing minerals) to Ca-P via reaction of desorbed P with $CaCO_3$ present in the soils, during NaOH extraction. In (b), the overestimation of Ca-P is caused by reaction between exchangeable Ca^{2+} and desorbed P and ternary surface complexes, such as ≡Fe-PO_4-Ca may form as intermediates. In (c), P is occluded by poorly crystalline minerals, which may not be dissolved by 0.1 M NaOH but dissolvable by 1 M HCl, leading to overestimation of Ca-P. In (d), P is occluded by well-crystallized minerals and can be dissolved by neither NaOH nor 1 M HCl. The occluded P could be incorporated into the mineral crystal structure or physically trapped by mineral particle aggregates.

found in P_{occ} for 1-ky (19%) and 3000-ky (12%) SAGA soils and 3000-ky Merced soil (15%; Table S3).

Phosphorus Speciation of Concentrated HCl Extraction Residues. To improve our understanding of the nature of P_{occ}, a C-HCl extraction was further conducted on the D-HCl residue. Compared to the D-HCl residue P spectra, the spectra of the C-HCl residue showed more pronounced Ca-P features for the 1-ky SAGA soil (Figure 2d), consistent with increased Ca-P proportion from 14 to 22% after C-HCl extraction (Table S3). The spectra of D-HCl and C-HCl residues were almost identical for the 55-ky SAGA soil (Figure 2d), consistent with the slight change of the P speciation in these residues (Table S3). The whiteline peak position of the D-HCl residue spectra for the 750- and 3000-ky SAGA soils did not change after the extraction; however, based on the relative intensity of normalized reference spectra, the substantial decrease of peak heights for both soils (Figure 2d) suggests more P_o in the C-HCl residues. This result is consistent with the corresponding increase of P_o from 6 to 22% for the 750-ky soil and 12 to 19% for the 3000-ky soil (Table S3). As for Merced soils, the low quality of C-HCl residue spectra (data not shown) prevented a detailed analysis of the changes in P speciation with extraction.

Speciation of the P Extracted by SCE. For the SAGA soils, the LCF analysis was conducted on the D-HCl-difference spectra (i.e., the difference in spectra of the residues before and after D-HCl extraction) and not on the NaOH-difference spectra due to their poor spectra quality (Figures 3a and S5a).

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For the Merced soils, the NaOH-difference spectra had dips in front of the whiteline peaks (Figure S5b). Such abnormal features were due to the higher Ca-P concentration in the NaOH residues than in the raw soils, presumably because of the P redistribution during the $NaHCO_3$ and NaOH extractions. The distorted difference spectra also prevented further LCF analyses of these spectra.

The D-HCl-difference spectra of the two older SAGA soils strongly resembled that of apatite, while those of the two younger soils were dominated by the Fe/Al-P spectral features (Figure 3a). The D-HCl-extracted P is composed of almost exclusively Ca-P (97−100%) for the two older soils. In contrast, this fraction contained large proportions of Fe-P (54−66%) for the two younger soils (Table 2). The D-HCl difference spectra of Merced soils showed strong Ca-P spectral characteristics (Figure 3b) and thus, the D-HCl extracted P contained high proportions of Ca-P (84−92%), except for the 3-ky soil that contained only 43% Ca-P with significant (Fe + Al)-P (45%) (Table 2).

The C-HCl difference spectra reflected the speciation of C-HCl extracted P. For SAGA soils, the C-HCl-P was mainly (Fe + Al)-P (90−100%) with negligible Ca-P (Table 2), consistent with their spectral features (Figure 3c). The C-HCl difference spectra of the 1-ky SAGA soil and for the Merced soils were too noisy to fit using LCF (Figure S5c).

DISCUSSION

Although the misquantification of Ca-P led to inaccurate estimates of other P pools (e.g., intermediately available P pool, Figure 4a), our comparison of the SCE and XANES results is focused on Ca-P because the (Fe + Al)-P quantities cannot be determined by the modified Hedley extractions. The SCE-based Ca-P proportions are substantially higher than the XANES-based results for all SAGA and Merced soils except for the two older SAGA soils (Figure 4b). Note that the Ca-P pool derived from SCE here only includes D-HCl-P and not C-HCl-P because of the dominance of Fe/Al-P in the C-HCl-P fraction (Table 2). Although the uncertainties of P_o quantification may affect the quantifications of other pools,[20] the observed overestimations of Ca-P are caused mainly by either P redistribution during NaOH extraction or dissolution of Fe/Al oxides during D-HCl extraction, as discussed below.

Phosphorus Redistribution during Alkaline Extractions. Phosphorus redistribution during NaOH extraction was found previously only for soils containing $CaCO_3$ (Figure 5a).[23,44] However, with P K-edge XANES spectroscopy, we showed that P redistribution also occurred for soils free of $CaCO_3$, including all Merced soils and the 3000-ky SAGA soil. The P redistribution is the major reason for the overestimation of Ca-P by the extractions for these soils (Figure 4 and Table 1). One potential reason for the overestimation is formation of $CaCO_3$ precipitate from exchangeable Ca^{2+} and carbonate ion during $NaHCO_3$ extraction, on which phosphate adsorbs. To test the possibility, we added 750 μg of Ca^{2+} (3 times the averaged soil exchangeable Ca^{2+}) to 30 mL of 0.5 M $NaHCO_3$ but no precipitation was visually observed, suggesting that $CaCO_3$ did not form and thus P adsorption on $CaCO_3$ can be excluded. A previous study showed that high exchangeable Ca^{2+} can decrease $NaHCO_3$−P_i for lime ($Ca(OH)_2$)-amended soils due to formation of Ca phosphates.[45] We hypothesized that Ca phosphates also formed from precipitation between exchanged Ca^{2+} and desorbed phosphate, leading to overestimation of Ca-P. To test this hypothesis, either Ca^{2+} or phosphate, or both, were added during the $NaHCO_3$ extractions of both 1-ky SAGA and 3-ky Merced soils. Results showed that adding Ca^{2+} alone did not change P concentrations during $NaHCO_3$ extraction (Text S4 and Table S4), indicating that the desorbed P was not precipitated by dissolved Ca^{2+}.

The high Ca-P proportion in the $NaHCO_3$-extraction residues may be explained by the following mechanisms. The pH (pH 8.5) of the $NaHCO_3$ solution was not high enough and thus only able to remove phosphate weakly (likely physically) adsorbed on mineral surfaces,[19] leaving behind strongly (or chemically) adsorbed phosphate (Figure 5b). The exchangeable Ca^{2+} released into solution could possibly readsorb onto the strongly surface-bound phosphate to form >Fe/Al-PO_4-Ca or >Fe/Al-PO_4-Ca-PO_4 surface complexes. Their formation is suggested by the strong shifts of the whiteline positions to the lower energy but weak Ca-P shoulder feature of the $NaHCO_3$-residues (Figure 2) because phosphate is bound to only one or two Ca atoms in these complexes, fewer than those in the structure of well-crystallized Ca phosphates. Formation of such complexes was also speculated to occur on Fe oxide surfaces at pH 8−14 in recent studies.[46,47]

Upon the NaOH extraction, despite less new Ca-P formed, these surface complexes likely transformed to more crystallized Ca-P precipitates, supported by the strong Ca-−P shoulder feature (Figure 2), consistent with favored formation of Ca phosphates at high pH.[47] The Ca phosphates were likely poorly crystallized and might transform to nanohydroxyapatite by physical mixing during NaOH extractions.[47−49] The processes described above could well explain how Ca-P was overestimated by $NaHCO_3$ and NaOH extractions for some of the soil samples examined in the present study. According to this mechanism, NaOH extraction alone (i.e., without the preceding $NaHCO_3$ extraction step) must also lead to overestiamtion of Ca-P. In fact, McLaren et al.[50] indicated that 0.1 M NaOH treatment might result in more Ca-P in soil based on the XANES spectral change after the treatment, although the spectra were too poor to make a reliable evaluation.

Dissolution of Fe/Al−P in the 1 M HCl Extraction. The overestimation of Ca-P for the two younger SAGA soils is not caused by P redistribution during the alkaline extractions but by dissolution of Fe/Al-P by D-HCl. The extraction of Fe/Al-P by D-HCl (Table 2) indicates that the preceding NaOH extraction step did not remove these Fe/Al-P. Because phosphate does not desorb from mineral surfaces under acidic conditions,[15] the removed Fe/Al-P can be ascribed to dissolution of poorly crystallized Fe/Al oxides (e.g., ferrihydrite, nanogoethite, nanohematite, allophane, and imogolite), releasing P that was occluded by these minerals (Figure 5c).

The phosphate should be occluded rather than surface-adsorbed P because surface-adsorbed P would otherwise have been removed by NaOH extraction. In addition, if the P adsorbs on mineral surfaces, it would likely form >Fe/Al-PO_4-Ca ternary complexes during the alkaline extractions, like other SAGA and Merced soils, which, however, were not observed by XANES spectroscopy (Tables 1, 2 and Figure 2). A recent laboratory study also found that phosphate can be occluded by ferrihydrite aggregates.[51] The Fe/Al oxides must be poorly crystallized rather than well-crystallized because only the former can be readily dissolved by D-HCl.[52] Significant correlations between D-HCl-Fe and Fe_{ox} and D-HCl-Al and

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Al_{ox} (Table S5) also support the proposition of the dissolution of poorly crystalline minerals during the D-HCl extraction. Moreover, in the D-HCl extract, but not the C-HCl extract, P is correlated to Fe, Al, and Ca (Table S5). However, the changes of specific P species in the residues did not necessarily correlate with the removed Al, Fe, and Ca because these elements had much higher concentrations than P in the extracts (Table S6) and the majority of them were not bound to P in the soil.

Dependence of Misquantification on Soil Properties. The present study demonstrates that the degree and cause of the misquantification of Ca-P and other P_i pools by the modified Hedley SCE are soil-specific (i.e., depending on associated soil properties). Our results suggest that it is the form of Fe- or Al-P, either surface-adsorbed by Fe/Al minerals (poorly crystalline or well-crystallized) or occluded by poorly crystalline Fe/Al minerals, that largely determines the accuracy of the alkaline and D-HCl extractions. High concentrations of well-crystallized Fe/Al minerals and low concentrations of poorly crystalline ones in the Merced soil and 3000-ky SAGA soil (Table S1) led to formation of surface-adsorbed phosphate or occluded phosphate by the well-crystallized minerals. The surface-adsorbed P could form Ca-P during the $NaHCO_3$ and NaOH extractions. By contrast, a high amount of poorly crystalline Fe/Al minerals and a low amount of well-crystallized ones, such as those occurring in the 1- and 55-ky SAGA soils, favor the formation of occluded P by the poorly crystalline minerals. They can neither be removed by NaOH nor react with exchangeable Ca^{2+} to form ternary surface complexes.

The differences in the Fe- and Al-P forms may be largely caused by the variations in soil weathering degree and the nature of the parent material. In poorly weathered soils (e.g., 1- and 55-ky SAGA soils), especially developed on basalt (e.g., andisols), a large amount of poorly crystalline Fe/Al minerals could occlude a portion of the associated P as a result of diffusive penetration or within coatings and concretions of the Fe/Al minerals.[53,54] As soil continues to weather, poorly crystalline Fe/Al minerals transform to well-crystallized ones that cannot be dissolved readily by D-HCl and thus P becomes strongly occluded (Figure 5d). However, these mechanisms cannot explain the comparable Ca-P results of XANES and extraction for 750-ky SAGA soil, suggesting that unknown soil properties, other than discussed above, could also affect the accuracies of SCE. A future study to examine a larger set of soil samples with diverse properties is warranted.

Speciation of Occluded P. The occlusion of P by well-crystallized minerals led to limited bioavailability in soils.[55,56] Whether P_{occ} could become biologically available over long time periods is partially controlled by its chemical nature.[1,24] However, the chemical nature of P_{occ} had remained ambiguous and long been speculated to be Fe-P, Al-P, or P_o with varying relative contributions based on SCE.[24,53,57−59] Previously, by using P K-edge XANES spectroscopy, the P_{occ} pool was found to be Fe-P without P_o[30] or both Fe-P and Ca-P[54] in agricultural soils. Our study verified the speculations of SCEs and demonstrated that P_{occ} was dominated by Fe/Al-P (66−90%) with less contribution from P_o and Ca-P. The occlusion of Ca-P, such as in 1-ky SAGA soil, was likely due to the apatite occlusion by minerals of high weathering resistance, such as hypersthene, magnetite, and ilmenite.[1,56] Our study highlights that the strategies for biota and nutrient management to utilize P_{occ} are soil-specific. For example, Fe oxides, but not Al oxides, can be reductively dissolved under reducing conditions, releasing P associated with the oxides.[60,61]

Environmental Implications. As major P fractionation techniques, SCE schemes have been widely used to assess P dynamics in soils and inform soil nutrient management. Hence, understanding the accuracy of SCE is crucial. Our study showed that misquantification of the major soil P pools can occur across a diverse suite of soils regardless of the presence or absence of $CaCO_3$. Although this study examined only the modified Hedley extraction, the results may apply to other SCE schemes as well because alkaline and acid extractions are used in almost all extraction schemes.[17−19] The misquantification of Ca-P and other pools raises concerns for any further analyses of extracted P and their data interpretation, such as for phosphate oxygen isotope analyses on NaOH and HCl extracted P.[26,62−65] Our results suggest that the widely accepted Walker and Syers model (Figure S6), which describes P biogeochemical transformation during ecosystem development,[24,56] may not be quantitatively testable using SCE due to the intrinsic uncertainties of SCE in quantifying P pools. Overall, SCE should be used cautiously for studying soil P dynamics and assessing potentials for P loss from soils to aquatic ecosystems leading to eutrophication.[66] Only a few soils of a limited number of different properties were examined in the present study, and other types of soils need to be tested in the future. Future studies are also warranted to develop new extraction schemes or modifying the existing ones. Our study suggests that uncertainties of other widely used P extraction techniques, such as the sequential extraction method for aquatic sediments (i.e., SEDEX), need to be evaluated using XANES spectroscopy and samples with diverse properties.[11,67]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.9b05278.

Details about the measurements of exchangeable Ca^{2+} and pedogenic Fe and Al, modified Hedley sequential extractions, the Ca^{2+} and phosphate precipitation experiment, some XANES spectra and fits, and the Walker and Syers model plots (PDF)

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Notes

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■ REFERENCES

(1) Selmants, P. C.; Hart, S. C. Phosphorus and soil development: Does the Walker and Syers model apply to semiarid ecosystems? *Ecology* **2010**, *91*, 474−484.
(2) Sharpley, A. Managing agricultural phosphorus to minimize water quality impacts. *Sci. Agric.* **2016**, *73*, 1−8.
(3) Cross, A. F.; Schlesinger, W. H. A literature review and evaluation of the Hedley fractionation: applications to the biogeochemical cycle of soil phosphorus in natural ecosystems. *Geoderma* **1995**, *64*, 197−214.
(4) Johnson, A. H.; Frizano, J.; Vann, D. R. Biogeochemical implications of labile phosphorus in forest soils determined by the Hedley fractionation procedure. *Oecologia* **2003**, *135*, 487−499.
(5) Yang, X.; Post, W. M. Phosphorus transformations as a function of pedogenesis: a synthesis of soil phosphorus data using Hedley fractionation method. *Biogeosciences* **2011**, *8*, 2907−2916.
(6) Negassa, W.; Leinweber, P. How does the Hedley sequential phosphorus fractionation reflect impacts of land use and management on soil phosphorus: A review. *J. Plant Nutr. Soil Sci.* **2009**, *172*, 305−325.
(7) Hou, E.; Tan, X.; Heenan, M.; Wen, D. A global dataset of plant available and unavailable phosphorus in natural soils derived by Hedley method. *Sci. Data* **2018**, *5*, No. 180166.
(8) Lehmann, J.; Lan, Z.; Hyland, C.; Sato, S.; Solomon, D.; Ketterings, Q. M. Long-term dynamics of phosphorus forms and retention in manure-amended soils. *Environ. Sci. Technol.* **2005**, *39*, 6672−6680.
(9) Li, W.; Joshi, S. R.; Hou, G.; Burdige, D. J.; Sparks, D. L.; Jaisi, D. P. Characterizing phosphorus speciation of Chesapeake Bay sediments using chemical extraction, ^{31}P NMR, and X-ray absorption fine structure spectroscopy. *Environ. Sci. Technol.* **2015**, *49*, 203−211.
(10) Eger, A.; Almond, P. C.; Condron, L. M. Phosphorus fertilization by active dust deposition in a super-humid, temperate environment—Soil phosphorus fractionation and accession processes. *Global Biogeochem. Cycles* **2013**, *27*, 108−118.
(11) Zhang, Z.; Goldstein, H. L.; Reynolds, R. L.; Hu, Y.; Wang, X.; Zhu, M. Phosphorus speciation and solubility in aeolian dust deposited in the interior American West. *Environ. Sci. Technol.* **2018**, *52*, 2658−2667.
(12) Bray, R. H.; Kurtz, L. Determination of total, organic, and available forms of phosphorus in soils. *Soil Sci.* **1945**, *59*, 39−46.
(13) Hedley, M.; Stewart, J.; Chauhan, B. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. *Soil Sci. Soc. Am. J.* **1982**, *46*, 970−976.
(14) Olsen, S. R.; Cole, C. V.; Watanabe, F. S.; Dean, L. A. *Estimation of Available Phosphorus in Soils by Extraction with Sodium Bicarbonate*; U.S. Department of Agriculture: Washington, DC, 1954.
(15) Tiessen, H.; Moir, J. Characterization of Available P by Sequential Extraction. *Soil Sampling and Methods of Analysis*; Taylor & Francis Group, 1993; Vol. 7, pp 5−229.
(16) Walker, T.; Adams, A. Studies on soil organic matter. I. Influence of phosphorus content of parent materials on accumulations of carbon, nitrogen, sulfur and organic phosphorus in grassland soils. *Soil Sci.* **1958**, *85*, 307−318.
(17) Pierzynski, G. M.; McDowell, R. W.; SIMS, T. J. Chemistry, Cycling, and Potential Movement of Inorganic Phosphorus in Soils. In *Phosphorus: Agriculture and the Environment*;Westermann, D. T., Ed.; American Society of Agronomy, Crop Science Society of America, Soil Science Society of America: Madison, WI, 2005; pp 53−86.
(18) Soinne, H. Extraction Methods in Soil Phosphorus Characterisation: Limitations and Applications. University of Helsinki: Helsinki, 2009.
(19) Moir, J.; Tiessen, H. Characterization of Available P by Sequential Extraction. *Soil Sampling and Methods of Analysis*, 2nd ed; CRC Press, 2007.
(20) Condron, L. M.; Newman, S. Revisiting the fundamentals of phosphorus fractionation of sediments and soils. *J. Soils Sediments* **2011**, *11*, 830−840.
(21) Yang, X.; Post, W. M.; Thornton, P. E.; Jain, A. The distribution of soil phosphorus for global biogeochemical modeling. *Biogeosciences* **2013**, *10*, 2525−2537.
(22) Wu, Y.; Prietzel, J.; Zhou, J.; Bing, H.; Luo, J.; Yu, D.; Sun, S.; Liang, J.; Sun, H. Soil phosphorus bioavailability assessed by XANES and Hedley sequential fractionation technique in a glacier foreland chronosequence in Gongga Mountain, Southwestern China. *Sci. China: Earth Sci.* **2014**, *57*, 1860−1868.
(23) Benzing, P.; Richardson, C. J. $CaCO_3$ causes underestimation of NaOH extractable phosphorus in sequential fractionations. *Soil Sci.* **2005**, *170*, 802−809.
(24) Crews, T. E.; Kitayama, K.; Fownes, J. H.; Riley, R. H.; Herbert, D. A.; Mueller-Dombois, D.; Vitousek, P. M. Changes in soil phosphorus fractions and ecosystem dynamics across a long chronosequence in Hawaii. *Ecology* **1995**, *76*, 1407−1424.
(25) Schlesinger, W. H.; Bruijnzeel, L. A.; Bush, M. B.; Klein, E. M.; Mace, K. A.; Raikes, J. A.; Whittaker, R. J. The biogeochemistry of phosphorus after the first century of soil development on Rakata Island, Krakatau, Indonesia. *Biogeochemistry* **1998**, *40*, 37−55.
(26) Helfenstein, J.; Tamburini, F.; von Sperber, C.; Massey, M. S.; Pistocchi, C.; Chadwick, O. A.; Vitousek, P. M.; Kretzschmar, R.; Frossard, E. Combining spectroscopic and isotopic techniques gives a dynamic view of phosphorus cycling in soil. *Nat. Commun.* **2018**, *9*, No. 3226.
(27) Prietzel, J.; Dümig, A.; Wu, Y.; Zhou, J.; Klysubun, W. Synchrotron-based P K-edge XANES spectroscopy reveals rapid changes of phosphorus speciation in the topsoil of two glacier foreland chronosequences. *Geochim. Cosmochim. Acta* **2013**, *108*, 154−171.

(28) Gu, C.; Hart, S. C.; Turner, B.; Hu, Y.; Meng, Y.; Zhu, M. Aeolian dust deposition and the perturbation of phosphorus transformations during long-term ecosystem development in a cool, semi-arid environment. *Geochim. Cosmochim. Acta* **2019**, *246*, 498−514.
(29) Hesterberg, D. Macroscale Chemical Properties and X-Ray Absorption Spectroscopy of Soil Phosphorus. In *Developments in Soil Science*; Singh, B.; Gräfe, M., Eds.; Elsevier, 2010; Chapter 11, Vol. *34*, pp 313−356.
(30) Kar, G.; Hundal, L. S.; Schoenau, J. J.; Peak, D. Direct chemical speciation of P in sequential chemical extraction residues using P K-edge X-ray absorption near-edge structure spectroscopy. *Soil Sci.* **2011**, *176*, 589−595.
(31) Kruse, J.; Leinweber, P. Phosphorus in sequentially extracted fen peat soils: A K-edge X-ray absorption near-edge structure (XANES) spectroscopy study. *J. Plant Nutr. Soil Sci.* **2008**, *171*, 613−620.
(32) Ajiboye, B.; Akinremi, O. O.; Hu, Y.; Flaten, D. N. Phosphorus speciation of sequential extracts of organic amendments using nuclear magnetic resonance and X-ray absorption near-edge structure spectroscopies. *J. Environ. Qual.* **2007**, *36*, 1563−1576.
(33) Doetterl, S.; Berhe, A. A.; Arnold, C.; Bodé, S.; Fiener, P.; Finke, P.; Fuchslueger, L.; Griepentrog, M.; Harden, J.; Nadeu, E.; et al. Links among warming, carbon and microbial dynamics mediated by soil mineral weathering. *Nat. Geosci.* **2018**, *11*, 589.
(34) Bullen, T.; White, A.; Blum, A.; Harden, J.; Schulz, M. Chemical weathering of a soil chronosequence on granitoid alluvium: II. Mineralogic and isotopic constraints on the behavior of strontium. *Geochim. Cosmochim. Acta* **1997**, *61*, 291−306.
(35) White, A. F.; Schulz, M. S.; Vivit, D. V.; Blum, A. E.; Stonestrom, D. A.; Harden, J. W. Chemical weathering rates of a soil chronosequence on granitic alluvium: III. Hydrochemical evolution and contemporary solute fluxes and rates. *Geochim. Cosmochim. Acta* **2005**, *69*, 1975−1996.
(36) Wang, J.; Wu, Y.; Zhou, J.; Bing, H.; Sun, H.; Luo, J.; Pu, S. Air-drying changes the distribution of Hedley phosphorus pools in forest soils. *Pedosphere* **2017**, DOI: 10.1016/S1002-0160(17)60456-9.
(37) Quesada, C. A.; Lloyd, J.; Schwarz, M.; Patiño, S.; Baker, T. R.; Czimczik, C.; Fyllas, N. M.; Martinelli, L.; Nardoto, G. B.; Schmerler, J.; Santos, A. J. B.; Hodnett, M. G.; Herrera, R.; Luizão, F. J.; Arneth, A.; Lloyd, G.; Dezzeo, N.; Hilke, I.; Kuhlmann, I.; Raessler, M.; Brand, W. A.; Geilmann, H.; Moraes Filho, J. O.; Carvalho, F. P.; Araujo Filho, R. N.; Chaves, J. E.; Cruz Junior, O. F.; Pimentel, T. P.; Paiva, R. Variations in chemical and physical properties of Amazon forest soils in relation to their genesis. *Biogeosciences* **2010**, *7*, 1515−1541.
(38) Zhou, J.; Wu, Y.; Prietzel, J.; Bing, H.; Yu, D.; Sun, S.; Luo, J.; Sun, H. Changes of soil phosphorus speciation along a 120-year soil chronosequence in the Hailuogou Glacier retreat area (Gongga Mountain, SW China). *Geoderma* **2013**, *195-196*, 251−259.
(39) Turner, B. L.; Laliberté, E. Soil development and nutrient availability along a 2 million-year coastal dune chronosequence under species-rich mediterranean shrubland in southwestern Australia. *Ecosystems* **2015**, *18*, 287−309.
(40) Ajiboye, B.; Akinremi, O. O.; Jürgensen, A. Experimental validation of quantitative XANES analysis for phosphorus speciation. *Soil Sci. Soc. Am. J.* **2007**, *71*, 1288−1291.
(41) Prietzel, J.; Klysubun, W.; Werner, F. Speciation of phosphorus in temperate zone forest soils as assessed by combined wet-chemical fractionation and XANES spectroscopy. *J. Plant Nutr. Soil Sci.* **2016**, *179*, 168−185.
(42) Eriksson, A. K.; Hesterberg, D.; Klysubun, W.; Gustafsson, J. P. Phosphorus dynamics in Swedish agricultural soils as influenced by fertilization and mineralogical properties: Insights gained from batch experiments and XANES spectroscopy. *Sci. Total Environ.* **2016**, *566−567*, 1410−1419.
(43) Baumann, K.; Glaser, K.; Mutz, J.-E.; Karsten, U.; MacLennan, A.; Hu, Y.; Michalik, D.; Kruse, J.; Eckhardt, K.-U.; Schall, P.; Leinweber, P. Biological soil crusts of temperate forests: Their role in P cycling. *Soil Biol. Biochem.* **2017**, *109*, 156−166.
(44) De Groot, C. J.; Golterman, H. L. Sequential fractionation of sediment phosphate. *Hydrobiologia* **1990**, *192*, 143−148.
(45) Sorn-Srivichai, P.; Tillman, R. W.; Syers, J. K.; Cornforth, I. S. The effect of soil pH on olsen bicarbonate phosphate values. *J. Sci. Food Agric.* **1984**, *35*, 257−264.
(46) Antelo, J.; Arce, F.; Fiol, S. Arsenate and phosphate adsorption on ferrihydrite nanoparticles. Synergetic interaction with calcium ions. *Chem. Geol.* **2015**, *410*, 53−62.
(47) Zhang, Y.; She, X.; Gao, X.; Shan, C.; Pan, B. Unexpected favorable role of Ca^{2+} in phosphate removal by using nanosized ferric oxides confined in porous polystyrene beads. *Environ. Sci. Technol.* **2019**, *53*, 365−372.
(48) Kitano, Y.; Okumura, M.; Idogaki, M. Uptake of phosphate ions by calcium carbonate. *Geochem. J.* **1978**, *12*, 29−37.
(49) Li, W.; Xu, W.; Parise, J. B.; Phillips, B. L. Formation of hydroxylapatite from co-sorption of phosphate and calcium by boehmite. *Geochim. Cosmochim. Acta* **2012**, *85*, 289−301.
(50) McLaren, T. I.; Guppy, C. N.; Tighe, M. K.; Schefe, C. R.; Flavel, R. J.; Cowie, B. C. C.; Tadich, A. Validation of soil phosphate removal by alkaline and acidic reagents in a Vertosol soil using XANES spectroscopy. *Commun. Soil. Sci. Plant Anal.* **2015**, *46*, 1998−2017.
(51) Santoro, V.; Martin, M.; Persson, P.; Lerda, C.; Said-Pullicino, D.; Magnacca, G.; Celi, L. Inorganic and organic P retention by coprecipitation during ferrous iron oxidation. *Geoderma* **2019**, *348*, 168−180.
(52) Chao, T.; Zhou, L. Extraction techniques for selective dissolution of amorphous iron oxides from soils and sediments. *Soil Sci. Soc. Am. J.* **1983**, *47*, 225−232.
(53) Velásquez, G.; Ngo, P.-T.; Rumpel, C.; Calabi-Floody, M.; Redel, Y.; Turner, B. L.; Condron, L. M.; de la Luz Mora, M. Chemical nature of residual phosphorus in Andisols. *Geoderma* **2016**, *271*, 27−31.
(54) Luo, L.; Ma, Y.; Sanders, R. L.; Xu, C.; Li, J.; Myneni, S. C. B. Phosphorus speciation and transformation in long-term fertilized soil: evidence from chemical fractionation and P K-edge XANES spectroscopy. *Nutr. Cycl. Agroecosyst.* **2017**, *107*, 215−226.
(55) Kitayama, K.; Majalap-Lee, N.; Aiba, S.-i. Soil phosphorus fractionation and phosphorus-use efficiencies of tropical rainforests along altitudinal gradients of Mount Kinabalu, Borneo. *Oecologia* **2000**, *123*, 342−349.
(56) Walker, T. W.; Syers, J. K. The fate of phosphorus during pedogenesis. *Geoderma* **1976**, *15*, 1−19.
(57) Dobermann, A.; George, T.; Thevs, N. Phosphorus fertilizer effects on soil phosphorus pools in acid upland soils. *Soil Sci. Soc. Am. J.* **2002**, *66*, 652−660.
(58) Hashimoto, Y.; Watanabe, Y. Combined applications of chemical fractionation, solution ^{31}P-NMR and P K-edge XANES to determine phosphorus speciation in soils formed on serpentine landscapes. *Geoderma* **2014**, *230−231*, 143−150.
(59) Smeck, N. E. Phosphorus dynamics in soils and landscapes. *Geoderma* **1985**, *36*, 185−199.
(60) McGroddy, M.; Silver, W.; De Oliveira, R.; De Mello, W.; Keller, M. Retention of phosphorus in highly weathered soils under a lowland Amazonian forest ecosystem. *J. Geophys. Res.: Biogeosci.* **2008**, *113*, No. G04012.
(61) Arai, Y.; Sparks, D. Phosphate reaction dynamics in soils and soil components: A multiscale approach. *Adv. Agron.* **2007**, *94*, 135−179.
(62) Zohar, I.; Shaviv, A.; Klass, T.; Roberts, K.; Paytan, A. Method for the analysis of oxygen isotopic composition of soil phosphate fractions. *Environ. Sci. Technol.* **2010**, *44*, 7583−7588.
(63) Angert, A.; Weiner, T.; Mazeh, S.; Sternberg, M. Soil phosphate stable oxygen isotopes across rainfall and bedrock gradients. *Environ. Sci. Technol.* **2012**, *46*, 2156−2162.

https://dx.doi.org/10.1021/acs.est.9b05278
Environ. Sci. Technol. XXXX, XXX, XXX−XXX

(64) Joshi, S. R.; Li, W.; Bowden, M.; Jaisi, D. P. Sources and pathways of formation of recalcitrant and residual phosphorus in an agricultural soil. *Soil Syst.* **2018**, *2*, No. 45.
(65) Tamburini, F.; Pfahler, V.; von Sperber, C.; Frossard, E.; Bernasconi, S. M. Oxygen isotopes for unraveling phosphorus transformations in the soil−plant system: A Review. *Soil Sci. Soc. Am. J.* **2014**, *78*, 38−46.
(66) Addiscott, T.; Brockie, D.; Catt, J.; Christian, D.; Harris, G.; Howse, K.; Mirza, N.; Pepper, T. Phosphate losses through field drains in a heavy cultivated soil. *J. Environ. Qual.* **2000**, *29*, 522−532.
(67) Ruttenberg, K. C. Development of a sequential extraction method for different forms of phosphorus in marine sediments. *Limnol. Oceanogr.* **1992**, *37*, 1460−1482.

https://dx.doi.org/10.1021/acs.est.9b05278
Environ. Sci. Technol. XXXX, XXX, XXX−XXX